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(54) **An electrical insulation improving agent, a method for its production and an improved electrical insulation material obtained therefrom**

(57) A method of treating zinc oxide powder comprises contacting zinc oxide powder with a silicon-containing compound having at least one silicon-bonded hydrogen atom per molecule, at from room temperature to 180°C for from one day to 10 minutes; and thereafter separating the treated zinc oxide powder from the residue of the silicon-containing compound.

A composition comprising a homogeneous mixture of an electrical insulating material and the treated zinc oxide powder constitutes an improved electrical insulation material.

The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

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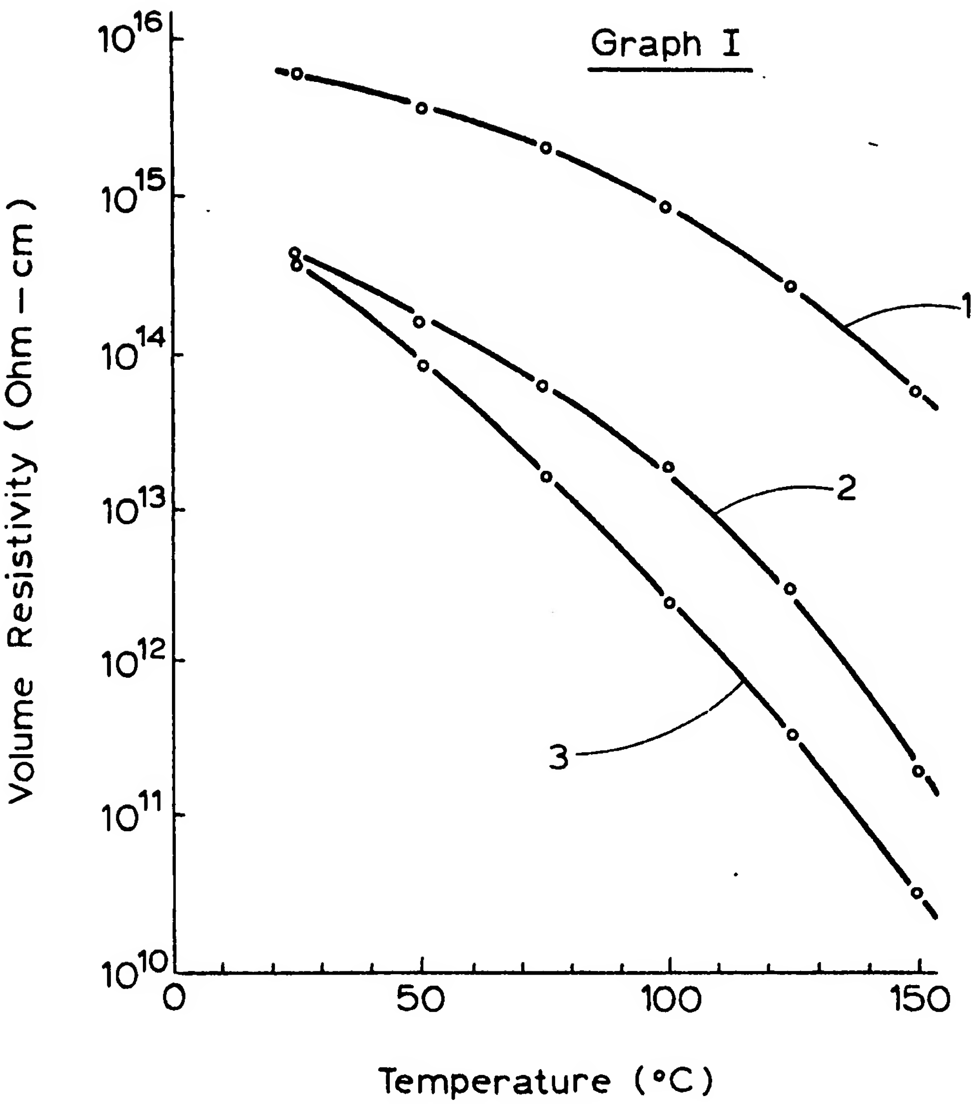
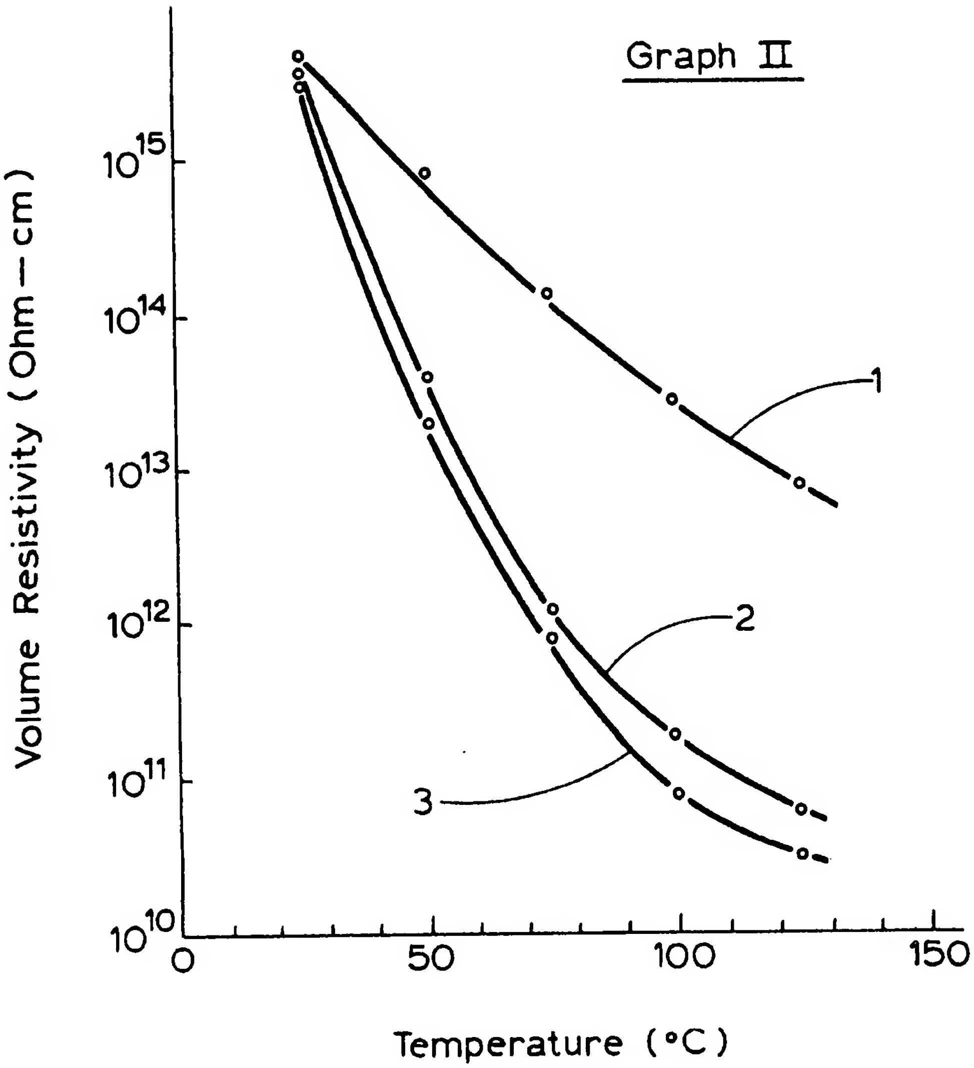

Graph I
Volume Resistivity (Ohm — cm)
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
0
50
100
150
Temperature (°C)
1
2
3

Fig .1



Graph II
Volume Resistivity (Ohm — cm)
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
0
50
100
150
Temperature (°C)
1
2
3

Fig. 2

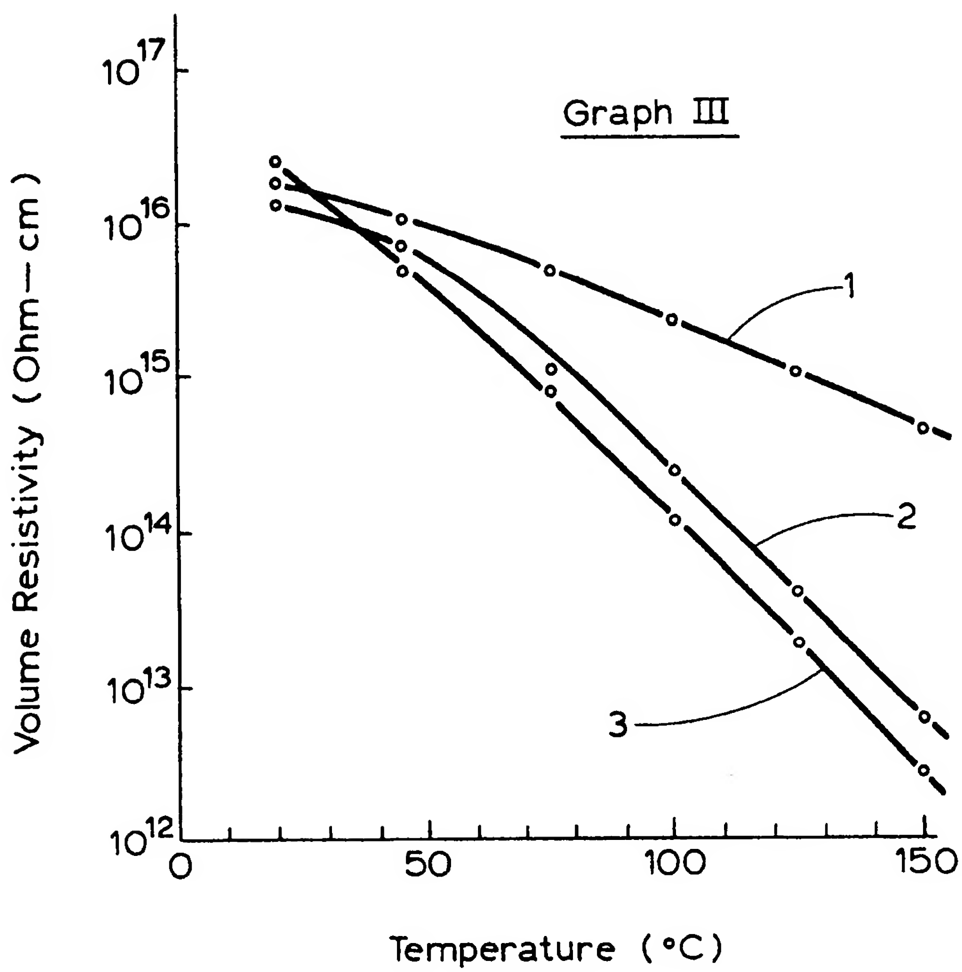

Graph III
Volume Resistivity (Ohm — cm)
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
0
50
100
150
Temperature (°C)
1
2
3

Fig. 3

SPECIFICATION

An electrical insulation improving agent, a method for its production and an improved electrical insulation material obtained therefrom.

This invention relates to an electrical insulation-improving agent for electrical insulating materials, to a method for its production and to an improved electrical insulation material obtained therefrom.

Electrical materials, especially electrical insulating materials, require further development in order to exhibit good properties in the small size, light-weight, high-capacity and high-reliability electrical applicances of today. Electrical insulating materials are indispensable in electrical appliances and have various configurations. The insulation material to which the method of this invention is applicable may be gaseous, liquid or solid.

Both organic and inorganic materials have been employed as electrical insulating materials. The materials in use at the present time are: materials which have been used for some time and are still viewed as important; materials materials which have been used for some time and have been improved; and new materials which have been developed recently. Examples of materials which have been in use for a long time are natural products such as mica, asbestos, rock crystal, sulfur, linseed oil, mineral oils, paraffin, asphalt and natural rubber. Materials which have recently been developed are materials based on synthetic organic polymers, such as synthetic rubbers, e.g. ethylene-propylene rubber, chloroprene rubber and styrene-butadiene rubber; curable resins, such as phenolic resins, epoxy resins, unsaturated polyester resins and silicone resins; and thermoplastic resins, such as polyethylene, polypropylene, ABS resins and fluorine-containing resins.

As noted above, various insulating materials with various configurations are used in many applications. Since the operational temperature and output capacity of an electrical device depend on the thermal resistance of the insulating material, insulating materials should be selected as required by the small size, light weight, high capacity and high reliability of electrical applicances.

Examples of insulating materials which are resistant to heat are inorganic materials such as mica, porcelain, glass, quartz and cement. However, these materials are limited in their applications due to their poor workabilities.

Insulating materials which do not exhibit the thermal resistance of the above-mentioned inorganic materials but which exhibit an excellent workability not found in inorganic materials include synthetic organic rubbers, such as ethylene-propylene rubber, chloroprene rubber, styrene-butadiene rubber, fluorocarbon rubber and silicone rubber; curable resins, such as phenolic resins, epoxy resins, unsaturated polyester resins, polyamides and silicone resins, and thermoplastic resins, such as polyesters, polyamides, vinyl chloride resins, polyethylene, polypropylene, polystyrene, polybutadiene, polysulfone, noryl resins, diallyl phthalate resin and polycarbonates. These materials are widely used in electrical applications at the present time.

However, the electrical insulating capacity of the above-mentioned electrical insulating materials quickly declines with increasing temperature with the result that the upper temperature limit for the electrical appliance is significantly restricted. This is a defect of the above-mentioned materials. For this reason, the development of an agent for improving the above-mentioned properties has been needed for some time.

Various methods were examined in order to discover a useful electrical insulation-improving agent which would reduce the decline in the electrical insulating capacity of electrical insulating materials due to temperature increases; in other words, an electrical insulation-improving agent which would improve the the electrical insulating property of electrical insulating materials over a wide temperature range, and especially at temperatures above room temperature. In particular, we have sought to provide such a useful electrical insulation-improving agent, a method for its production and an improved electrical insulation based thereon.

This invention describes an electrical insulation-improving agent for electrical insulating materials and a method for its production which are characterized by the following. Zinc oxide powder is treated with a compound which possesses at least one silicon-bonded hydrogen atom per molecule. Incorporation of the thus-treated zinc oxide into an electrical insulating material provides improved properties for the insulation.

The present invention relates to a method comprising contacting zinc oxide powder with a silicone-containing compound having at least one silicon-bonded hydrogen atom per molecule, the contacting being done at a temperature within the range of from room temperature to 180°C and for a period of time of from at least one day at room temperature to at least 10 minutes at 180°C, and thereafter separating the thus-treated zinc oxide powder from the residue of the silicone-containing compound.

The present invention further relates to a treated zinc oxide powder obtained by the method of this invention.

The present invention also relates to an improved electrical insulating material comprising a homogeneous mixture of the treated zinc oxide powder of this invention and an electrical insulating material.

The zinc oxide powder used in the method of this invention is any zinc oxide powder produced by the French method (indirect method), the American method (direct method) or the wet method. The particle size should be 0.1-1.10 μm. The purity of the zinc oxide should be greater than or equal to 97%. When a higher

insulating capacity is required, a purity higher than the above-mentioned purity is preferred.

The silicone-containing compound in which each molecule possesses at least one silicone-bonded hydrogen atom is an indispensable component and acts on the surface of the zinc oxide powder to improve the surface properties. Its average unit formula is

$$R_aH_bSiO_{\frac{4-a-b}{2}},$$

wherein R is an unsubstituted or substituted hydrocarbon group, a hydroxyl group or a hydrolysable group, *a* has a value of from 0 to, but not including, 4 and *b* has a value of from above 0 to, and including, 4.

The molecular shape of the silicone-containing compound is not critical and may be that of a simple compound, linear, branched linear, cyclic, branched cyclic, reticulated or network; however, it is usually linear or cyclic. The compound may be a homopolymer or copolymer. It should be liquid at room temperature.

Examples of the unsubstituted hydrocarbon group are methyl, ethyl, *n*propyl, octyl, cyclohexyl, phenyl and vinyl.

Examples of the substituted hydrocarbon group are tolyl, xylyl, benzyl, *p*-chlorophenyl, cyanoethyl and 3,3,3-trifluoropropyl.

Examples of the hydrolysable group are methoxy, ethoxy, *n*-propoxy, acetoxy, dialkyl ketoxime and alkylamino.

There is at least one silicone-bonded hydrogen atom per molecule; however, the number of such hydrogen atoms should be such that the value of *b* in the above formula is at least 0.05. Examples of suitable silicon-containing compounds are dimethylsilane, trimethysilane, trimethoxysilane, methyldiethoxysilane, a methylhydrogenpolysiloxane in which both ends are blocked with trimethylsiloxy groups, a dimethylpolysiloxane in which both ends are blocked with dimethylhydrogen siloxy groups, a methylhydrogensiloxane-dimethylsiloxane copolymer in which both ends are blocked with trimethylsiloxy groups, a methylhydrogen-polysiloxane in which both ends are blocked with dimethylhydrogensiloxy groups, a methylhydrogenpolysiloxane in which both ends are blocked with dimethyloctylsiloxy groups, tetramethyltetrahydrogen-cyclotetrasiloxane, a methylhydrogenpolysiloxane in which both ends are blocked with dimethylphenylsiloxy groups and methylphenylsiloxane-methylhydrogensiloxane copolymer in which both ends are blocked with dimethylphenylsiloxy groups.

The silicone-containing compound is preferably an organohydrogenpolysiloxane wherein the organic groups are unsubstituted hydrocarbon groups.

The zinc oxide powder can be contacted with the silicone-containing compound in any manner, such as in a dynamic manner, e.g. in a flowing or stirring apparatus, or in a static manner, e.g. by allowing the mixture of components to stand undisturbed.

When this contacting is carried out as a slurry of zinc oxide in an organic solvent, such as a hydrocarbon, e.g. toluene, xylene, hexane or heptane, which dissolves the silicone-containing compound, the surface of the zinc oxide is uniformly treated. Thus, this process is preferred.

The zinc oxide powder is allowed to remain in contact with the silicon-containing compound at room temperature for at least 1 day, and preferably 1-7 days, or at a temperature ranging from room temperature to 180°C, and preferably at 50-100°C, for at least 10 minutes, and preferably for a period of from 10 minutes to 24 hours.

The residue of the silicon-containing compound is subsequently separated from the treated zinc oxide powder. One method of removing the above-mentioned residue of the silicon-containing compound from the zinc oxide powder is by filtering or centrifuging, and subsequent washing of the filter cake with a hydrocarbon solvent for the residue of the silicon-containing compound.

The quantity of the above-mentioned silicon-containing compound used for the surface treatment of zinc oxide should be 1-30 parts by weight per 100 parts by weight of zinc oxide powder. When this value is less than 1 part by weight, the surface treatment is insufficient. On the other hand, when this value exceeds 30 parts by weight, the zinc oxide powder tends to coagulate.

When the treated zinc oxide powder is used as a component in an electrical insulating material, the decline in the electrical insulating capacity of the electrical insulation material due to an increase in temperature is significantly controlled. In other words, this agent improves the electrical insulating capacity of the insulating material over a wide temperature range, and especially in the temperature range above room temperature.

The amount of this electrical insulation-improving agent to be added to an insulating material is 5-300 wt% based on the weight of the electrical insulating material.

Electrical insulating materials which are appropriate candidates for the addition of this electrical insulation-improving agent includes natural organic materials such as mineral oils, paraffin, asphalt and natural rubber and synthetic organic materials. Materials which are solid at room temperature are preferred. Rubbers, curable resins and thermoplastic resins are the most preferred.

Examples of rubbers are natural rubber, isoprene rubber, chloroprene rubber, ethylene-propylene rubber, EPDM rubber, styrene-butadiene rubber, butyl rubber, butadiene rubber, acrylic rubber, urethane rubber, silicone rubber, fluorine-containing rubber, hypalon, epichlorohydrin rubber and epoxy rubber.

The curable resin may be a room-temperature curable resin or a thermosetting resin. Examples are phenolic resins, epoxy resins, unsaturated polyester resins, alkyd resins, silicone resins, polyurethane resins, melamine resins and polyimide resins.

Examples of the thermoplastic resins are polyethylene, polypropylene, polystyrene, polyamide, polyester, polyvinyl chloride, polycarbonate, poly(methyl methacrylate), polyacetal and fluorine-containing resins.

An electrical insulating material which contains an electrical insulation-improving agent produced by the method of this invention can be used as an electrical insulating material for various electrical parts, electronic parts, electrical appliances and electronic appliances. It is preferably used as an electrical insulating material for parts which are exposed to high temperatures.

The invention is now further explained, but not limited, by using illustrative examples. All parts and percentages are by weight unless otherwise stated. Viscosities were measured at 25°C.

Graphs I, II and III of the accompanying drawings are data displays of the relationship between volume resistivity and temperature. The ordinate values represent the volume resistivity and the abscissa values represent the temperature.

In each graph, curve 1 shows the volume resistivity of a cured composition produced by the method of this invention, curve 2 shows the volume resistivity of a cured composition in which untreated zinc oxide powder was used instead of suface-treated zinc oxide powder and curve 3 shows the volume resistivity for a cured composition of the resin alone.

Example 1

Zinc oxide powder (400 parts, purity: 99%, average particle size: 0.5 μm) was combined with xylene (700 parts). The resulting mixture was combined under agitation, with a methylhydrogenpolysiloxane (30 parts, viscosity: 10 cS) in which both ends were blocked with trimethylsiloxy groups. The mixture was agitated at 100°C for 1 hour under reflux. It was then filtered and the residue was washed with xylene and then dried.

A liquid epoxy resin, Chisso Nox 221 (trade mark) of Chisso Corp., chemical name: 3,4-epoxycyclohexylmethyl-(3,4-cyclohexane carboxylate) (100 parts) was combined with methyl hamic anhydride (80 parts) as the curing agent, ethylene glycol (4 parts) and the above-mentioned surface-treated zinc oxide powder (50 parts). The resulting mixture was homogeneously dispersed. The resin was then cured at 150°C for 24 hours to form a 1.0 mm thick sheet. The volume resistivity of this sheet was measured by the method of JIS C-2123.

For comparison examples, the volume resistivity was measured on compositions in which untreated zinc oxide powder had been used instead of the surface-treated zinc oxide and for the cured composition of the epoxy resin alone. The results are given in Graph I. The cured composition containing the surface-treated zinc oxide powder was clearly found to be excellent.

Example 2

Zinc oxide powder (400 parts, purity: 99%, average particle size: 0.5 μm) was combined with heptane (700 parts). The resulting mixture was combined with tetramethyltetrahydrogencyclotetrasiloxane (50 parts) while the mixture was being agitated. The mixture was agitated at 60°C for 3 hours under reflux. The mixture was filtered, and the residue was washed with heptane and then dried.

An unsaturated polyester resin (brand name) TVB-2122 from Toshiba Chem. Co., Ltd., 100 parts) was combined with curing agent TEC-9611 (1.0 part) and the above-mentioned surface-treated zinc oxide powder (30 parts). The resulting mixture was homogeneously dispersed. This composition was cured at 100°C for 1 hour. The volume resistivity of the cured composition was measured by the method of Example 1. For comparison, the volume resistivity for a cured composition in which untreated zinc oxide powder was used instead of surface-treated zinc oxide powder and the volume resistivity for a cured composition of the epoxy resin alone were measured. The results are given in Graph II.

The results showed that the cured composition containing surface-treated zinc oxide powder exhibited excellent properties.

Example 3

Zinc oxide powder (100 parts, purity: 99%, average particle size 0.5 μm) was combined with a copolymer (20 parts, viscosity: 100 cS) of dimethylsiloxane (80 mol%) and methylhydrogensiloxane (both ends were blocked with trimethylsiloxy groups). The resulting mixture was homogeneously mixed and then allowed to stand at 100°C for 1 hour. The mixture was filtered and the residue was thoroughly washed with xylene.

The above-mentioned surface-treated zinc oxide powder (50 parts) was combined with a silicone varnish composed of a methylphenylpolysiloxane resin (100 parts, silanol group content: 5%), xylene (100 parts) and an extremely small quantity of lead octoate as curing catalyst. The resulting mixture was uniformly dispersed. It was formed into a thin film which was subsequently allowed to stand at room temperature to evaporate the xylene. The sheet was cured at 180°C for 20 hours. The volume resistivity of the 1.0 mm thick cured sheet was measured by the method of Example 1.

For comparison examples, the volume resistivity of a cured composition in which untreated zinc oxide powder was used instead of surface-treated zinc oxide powder and the volume resistivity for the cured silicone varnish alone were measured by the same method. The results are given in Graph III. The cured composition containing the surface-treated zinc oxide powder was found to exhibit excellent properties.

Example 4

Ethylene-propylene terpolymer (100 parts, brand names: EPT-3045 from Mitsui Petrochem. Co., Ltd.) was combined with process oil (10 parts). The resulting mixture was thoroughly kneaded using a two-roll mill. The mixture was combined with a surface-treated zinc oxide powder (50 parts) identical to that used in Example 1. The resulting mixture was thoroughly kneaded using a two-roll mill, and then combined with dicumyl peroxide (4 parts). The mixture was again well kneaded. It was press vulcanized at 170°C under a pressure of 30 kg/cm^2 for 10 minutes to form a 1 mm thick sheet. This rubber sheet was heat treated in a hot-air circulating oven at 150°C for 3 hours. The volume resistivity of this sheet was measured by the method of JIS C-2123.

For comparison examples, the volume resistivity for a rubber sheet with a composition in which untreated zinc oxide powder was used instead of the surface-treated zinc oxide powder, and the volume resistivity for a rubber sheet with a composition in which talc was used instead of surface-treated zinc oxide powder was measured. The results are given in Table I below.

Example 5

Organopolysiloxane raw rubber (100 parts, $(CH_3)_2SiO$ unit: 99.8 mol% and $(CH_3)(CH_2{=}CH)SiO$ unit: 0.2 mol%) in which the ends were blocked with trimethylsilyl groups was combined with a surface-treated zinc oxide powder (30 parts) identical to those used in Example 2. The resulting mixture was thoroughly kneaded using a two roll mill and then combined with pasty 2,4-dichlorobenzoyl peroxide (2 parts, purity: 50%). The mixture was uniformly kneaded. This composition was press vulcanized at 120°C under a pressure of 30 kg/cm^2 for 10 minutes to form a 1 mm thick rubber sheet. This sheet was heat treated in a hot-air circulating oven at 200°C for 4 hours. The volume resistivity of the sheet was measured by the method of Example 4.

For comparison example, the volume resistivity was measured for a rubber sheet with a composition in which untreated zinc oxide powder was used instead of surface-treated zinc oxide powder. The results are given in Table II below.

Example 6

Commercial polycarbonate chips (100 parts) were melted at an elevated temperature under a nitrogen atmosphere. The melt was combined with a surface-treated zinc oxide powder (60 parts) identical with that used in Example 3. The resulting mixture was thoroughly agitated and then cooled to form a 1.0 mm thick sheet.

The volume resistivity of the sheet was measured by the method of JIS-C-2123 and was found to be 1.3×10^{17} ohm-cm at 25°C, 5.8×10^{16} ohm-cm at 100°C and 1.4×10^{16} ohm-cm at 140°C. The volume resistivity for a sheet of polycarbonate resin alone was 9×10^{16} ohm-cm at 100°C and 7×10^{14} ohm-cm at 140°C.

TABLE I

Sample Composition (parts)	This invention	Comparison Example	Comparison Example
EPT - rubber	100	100	100
Process oil	10	10	10
Zinc oxide	50 (Treated surface)	50 (untreated surface)	—
Talc	—	—	50
Dicumyl peroxide	4	4	4
Volume resistivity (ohm-centimetres)			
25°C	1.2×10^{16}	9.5×10^{15}	7.5×10^{15}
100°C	3.8×10^{15}	4.3×10^{14}	2.5×10^{14}
130°C	8.5×10^{14}	6.5×10^{13}	5.2×10^{13}

TABLE II

Sample Component (parts)	This Invention	Comparison Example
Polysiloxane raw rubber	100	100
Zinc oxide	30 (treated surface)	30 (untreated surface)
2,4-Dichlorobenzoyl peroxide	2	2
Volume resistivity (ohm-centimetres)		
25°C	4.0×10^{16}	2.5×10^{16}
100°C	1.1×10^{16}	8.2×10^{15}
150°C	3.4×10^{15}	2.5×10^{14}

CLAIMS

1. A method of treating zinc powder comprising contacting zinc oxide powder with a silicon-containing compound having at least one silicon-bonded hydrogen atom per molecule, said contacting being done at a temperature of from room temperature to 180°C and for a period of time of from at least one day at room temperature to at least 10 minutes at 180°C, and thereafter separating the thus-treated zinc oxide powder from the residue of the silicon-containing compound.
2. A method according to claim 1, wherein the zinc oxide powder has an average particle size of from 0.1 to 10 μm and a purity of at least 97 percent by weight, and the silicon-containing compound is an organohydrogenpolysiloxane.
3. A method according to claim 1 or 2, wherein 100 parts by weight of the zinc oxide powder are contacted with from 1 to 30 parts by weight of the silicon-containing compound.
4. A method according to claim 1, substantially as herein described with reference to the accompanying drawings and to any of the specific examples.
5. A treated zinc oxide powder obtained by the method of any of claims 1 to 4.
6. A composition comprising a homogeneous mixture of an electrical insulating material and the treated zinc oxide powder of claim 5.
7. The composition of claim 6, wherein the electrical insulating material is a rubber, a curable resin or a thermoplastic resin.
8. The composition of claim 6 or 7 which contains from 5 to 300 percent by weight of the treated zinc oxide based on the weight of the electrical insulating material.

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